

UDC 666.321

## PARTICULARS OF THE CHEMICAL MINERALOGICAL COMPOSITION AND PROPERTIES OF KAOLINS FROM BELORUSSIAN DEPOSITS

O. A. Sergievich,<sup>1</sup> E. M. Dyatlova,<sup>1,3</sup> G. N. Malinovskii,<sup>1</sup> S. E. Barantseva,<sup>1</sup> and R. Yu. Popov<sup>1</sup>

Translated from *Steklo i Keramika*, No. 3, pp. 25 – 31, March, 2012.

A comprehensive study of the compositions and properties of primary kaolins from the Sitnitsa and Dedovka deposits in the Republic of Belarus was performed. The mineralogical and chemical compositions, phase transformations during heating, dilatometric properties, and the properties of kaolin raw material were studied for individual fractions. A relation is established between the quality, structure, and physical-chemical properties, which made it possible to recommend the most effective methods of enriching the kaolin raw material studied.

**Key words:** kaolin, chemical-mineralogical and fractional composition, mullite, physical-chemical properties, enrichment methods.

Increasing the production scales of building and facing rock, for which mainly magmatic rock from Belarus, specifically, the deposits in the Mikashevichi and Zhitkovichi salients, serve as the raw material, requires the use of overburden rocks, represented mainly by kaolins. In the Republic of Belarus there are no operating deposits of kaolin clays, so that the problems of creating a domestic mineral-raw materials base of kaolin raw material and developing technologies for its reprocessing and deep enrichment are very topical.

It should be noted that kaolins from the Belorussian deposits differ by their structure and properties from high-quality kaolins from Ukraine and Russia. Four kaolin deposits (Sitnitsa, Dedovka, Berezina, Lyudenevichi) have been found on the territory of Belarus. These deposits are tied to sections of shallow bedding of crystalline rocks and are a product of the breakdown of gneisses, granite-gneisses, schists and granites and, as a rule, are primary and in individual cases secondary kaolins because of erosion and re-deposition. The considerable amount of mechanical inclusions, high content coloring oxides and other impurity components make for low quality of the raw material. Of greatest interest for practical use are kaolins from the Sitnitsa and Dedovka deposits.

The Sitnitsa deposit lies in Brest Oblast. The kaolins represent the weathered crust of gneisses and granite-gneisses

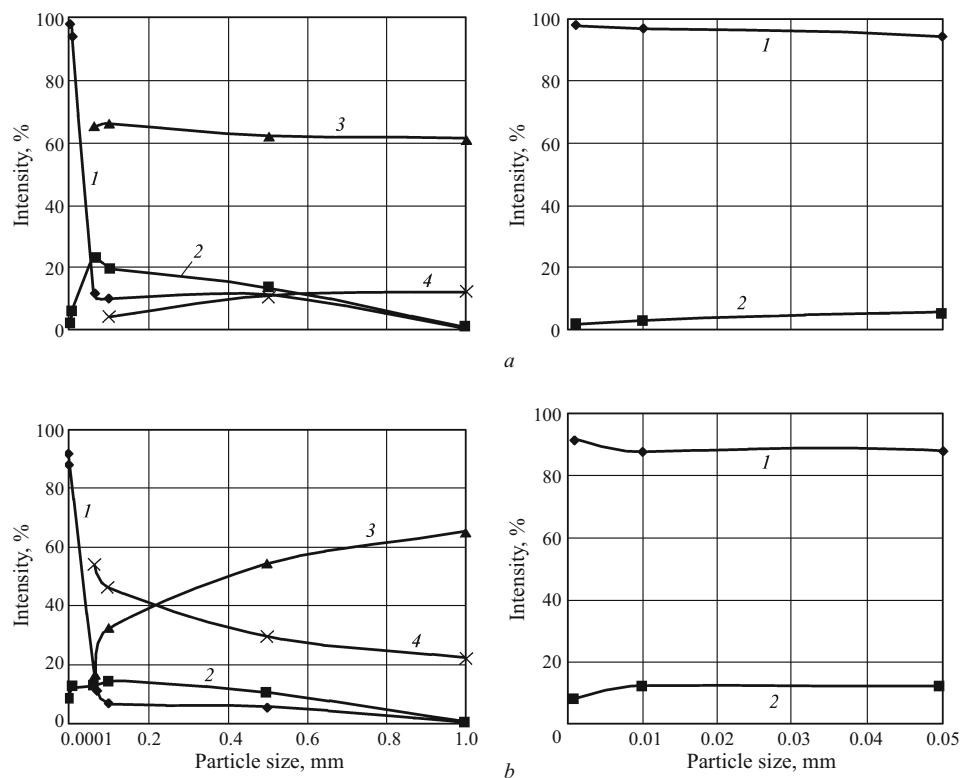
and they comprise a 2.0 – 9.1 m thick (average 3.6 m) sheet bed. They lie under sandy-clayey deposits with thickness 12.0 – 23.4 m. The proven reserves of primary kaolin-raw material in the Sitnitsa deposit comprise about  $2.53 \times 10^6$  tons. The macroscopic primary kaolins in Sitnitsa comprise clayey rock of grey color, greasy feel and weakly chlorinated with large inclusions of feldspar-quartz fragments, biotite flakes, quartz grains, and feldspar. The eastern part of the deposit lies within a planned quarry of building rock, so that for obtaining kaolin as a by-product this section has been explored in detail [1].

The Dedovka deposit lies in Gomel' Oblast and is represented by primary and secondary kaolins. The thickness of the deposit is 2.9 – 53.9 m and the bedding depth is 29.7 – 37.4 m. The overburden consists of sandy-clayey deposits. Secondary kaolins are embedded among glauconite-quartz sands at depth 28.3 – 33.0 m. The bed of secondary kaolins lies above the primary kaolins, repeating the latter's form, but it is somewhat larger with much thinner, 1.2 – 5.4 m. These are yellow-grey rocks with mechanical impurities of glauconite-quartz sand, muscovite, feldspar, and fragments of crystalline rock; a greenish tinge due to glauconite impurities is characteristic for secondary kaolins. The total reserves of primary kaolin raw material comprise  $7.02 \times 10^6$  tons and secondary kaolins amount to  $1.23 \times 10^6$  tons. Even though the secondary kaolins are contaminated with glauconite-quartz sands, the yield of enriched kaolin in them is somewhat higher (48.8% versus 28.4% for the primary kaolin); the chemical composition and technological properties are close [1].

<sup>1</sup> Government Enterprise, Scientific Research Institute of Building Materials, Minsk, Belarus.

<sup>2</sup> Belorussian State Technological University, Minsk, Belarus.

<sup>3</sup> E-mail: keramika@bstu.unibel.by.



**Fig. 1.** Intensity of diffraction peaks of crystalline phases versus the particle size of Sitnitsa (a) and Dedovka (b) kaolin: 1) kaolinite; 2) hydromica; 3) quartz; 4) microcline.

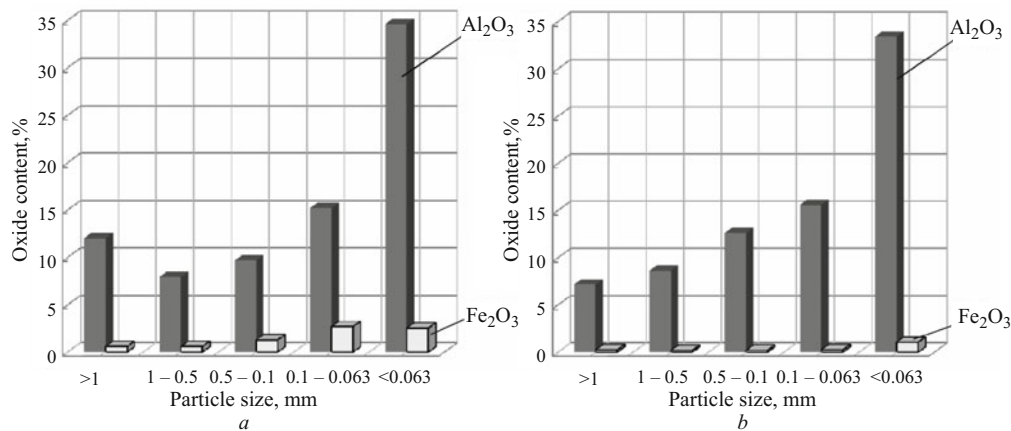
Thus far, for all intents and purposes, a detailed x-ray diffraction analysis of the kaolins in the indicated deposits has not been performed. At the same time, the presence and ratio (relative amounts) of the mineral phases present in the kaolins greatly affects the properties of the ceramic mixes and fired products. It has been established that the presence of definite mineral phases is directly related with the particle-size composition of the experimental samples of primary kaolins (Table 1).

According to x-ray phase analysis, results of which are presented in Fig. 1, the intensity of the diffraction peaks due to the impurity minerals — quartz and microcline — are directly related with the particle-size composition of the rock and differs somewhat for Sitnitsa and Dedovka kaolin, especially with respect to the content of the quartz component. It was established that the impurity minerals are contained in the  $> 1$  mm and  $1 - 0.063$  mm fractions; in addition, the maximum amount of free quartz in Sitnitsa kaolin lies in the  $1 - 0.1$  mm fraction and for Dedovka kaolin this is characteristic for  $> 1$  mm particles. Impurity microcline in Sitnitsa kaolin is appreciably represented in  $> 1$  mm particles; then its relative content decreases. The microcline in Dedovka kaolin is more finely dispersed, the maximum intensity of its diffraction peak is

characteristic for the  $0.063 - 0.1$  mm fraction. As particle size decreases, the amount of quartz decreases, more for Dedovka kaolin; in  $< 0.005$  mm particles in Sitnitsa and Dedovka kaolins, impurity minerals are absent and the phase composition of these particles is represented almost entirely by clay-forming minerals — kaolinites and hydromicas (muscovite, hydromica, illite), the content of the latter reaching its highest value in the  $0.1 - 0.063$  mm fraction.

**TABLE 1.** Phase Composition of Kaolin Raw Material by Fractions

Kaolin deposit	Particle size, mm	Fraction content, wt. %	Qualitative mineral composition by fractions			
			Kaolinite	Hydromica	Quartz	Microcline
Sitnitsa	$> 1$	8.53	Traces		Traces	
	$1 - 0.5$	23.47	+	+	+	+
	$0.5 - 0.1$	28.81	+	+	+	+
	$0.1 - 0.063$	4.40	+	+	+	—
	$0.063 - 0.005$	12.15	+	+	—	—
	$0.005 - 0.001$	10.94	+	+	—	—
	$< 0.001$	11.70	+	+	—	—
Dedovka	$> 1$	13.35	Traces	Traces	+	+
	$1 - 0.5$	10.42	+	+	+	+
	$0.5 - 0.1$	27.09	+	+	+	+
	$0.1 - 0.063$	9.54	+	+	+	+
	$0.063 - 0.005$	25.76	+	+	—	—
	$0.005 - 0.001$	6.30	+	+	—	—
	$< 0.001$	7.54	+	+	—	—



**Fig. 2.** Variation of the Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> content in different fractions of natural kaolins from the Sitnitsa (a) and Dedovka (b) deposits.

These data agree well with the results of fractional chemical analysis of Sitnitsa and Dedovka kaolins presented in Table 2. They attest to the fact that the highest amount of Al<sub>2</sub>O<sub>3</sub> is present in the < 0.063 mm fraction and this fraction is characterized by kaolinite content of about 90%. The oxide chemical composition of kaolins presented in Table 2 attests to a low Al<sub>2</sub>O<sub>3</sub> content and elevated Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O contents in their average sample, which limits the use of kaolin raw material from both deposits in refractory and porcelain manufacture. As the particle size of both rocks decreases the amount of Al<sub>2</sub>O<sub>3</sub> increases and reaches 33–34% in < 0.063 mm fractions, which are mainly represented by clay-forming minerals, while the impurity minerals are removed by large particles, which is clearly seen in Fig. 2.

As the data evidence, the chemical composition of the kaolins depends directly on the composition of the primary rocks. A characteristic feature of mineral from both deposits is a quite high K<sub>2</sub>O content, which attests to incomplete decomposition of feldspars and makes it possible to classify them as alkaline.

Thus, to eliminate impurities of quartz and parent rock from the indicated kaolins particles with sizes > 0.063 mm

must be separated from them. However, analysis of the data obtained shows that iron compounds will not be removed with the large fractions on enrichment, since they occur in their highest amount in fractions < 0.063 mm in the form of finely disperse iron-containing minerals as well as in an octahedral layer of the crystal lattice of clay minerals with isomorphic substitution  $\text{Al}^{3+} \rightarrow \text{Fe}^{3+}$ . In turn, this requires deeper purification of the raw material by chemical enrichment, which removes the oxides FeO and Fe<sub>2</sub>O<sub>3</sub> via the formation of water-soluble iron compounds, and subsequent washing.

Phase transformations occurring in the kaolins at temperatures 20–1200°C were studied by means of differential-thermal analysis of natural and enriched kaolins; the results are presented in Fig. 3.

The endo effects present on the DTA curves for Sitnitsa kaolin in the natural and enriched form at temperatures 27–110 and 110–145°C are due to the removal of hygroscopic moisture; the mass loss is 0.57% in the first endo effect and 0.13% in the second one.

The authors of [2] believe that the presence of an endo effect at temperatures of the order of 150°C is explained by

**TABLE 2.** Fractional Oxide Chemical Composition of Kaolin Raw Material

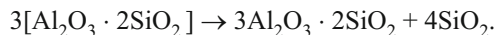
Kaolin deposit	Particles size, mm	Content, wt. %										
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	other
Sitnitsa	> 1	78.4	12.0	0.58	0.21	0.04	0.06	0.12	0.10	0.32	6.02	2.15
	1 – 0.5	84.9	7.94	0.57	0.19	–	0.06	0.15	0.11	0.22	4.60	1.26
	0.5 – 0.1	81.5	9.66	1.26	0.50	0.04	0.06	0.35	0.12	0.19	4.58	1.74
	0.1 – 0.063	71.2	15.2	2.69	0.93	0.06	0.06	0.68	0.25	0.15	5.28	3.50
	< 0.063	46.1	34.6	2.53	0.94	–	0.23	0.42	0.81	0.47	2.00	11.90
	Average sample	61.7	25.1	1.56	0.68	–	0.19	0.45	0.71	0.12	3.85	5.64
Dedovka	> 1	86.3	7.17	0.24	0.08	–	0.05	–	–	0.10	5.48	0.58
	1 – 0.5	83.6	8.65	0.19	0.07	–	0.04	–	–	0.12	6.55	0.78
	0.5 – 0.1	76.9	12.6	0.20	0.16	–	0.03	–	–	0.13	8.82	1.16
	0.1 – 0.063	72.2	15.6	0.25	0.18	–	0.04	–	–	0.15	9.47	2.11
	< 0.063	50.7	33.4	1.05	0.63	0.11	0.21	0.11	–	0.01	3.24	10.54
	Average sample	70.3	19.0	0.46	0.26	0.06	0.09	–	0.02	0.10	6.02	3.69

the presence of halloysite impurity, whose chemical composition is similar to that of kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ).

The substantial endo effect at temperatures 415–632°C is related with the destruction of the kaolinite lattice accompanying detachment and removal of crystallization water from it. In the process, metakaolinite  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  — an amorphous product with partial preservation of the structure of the kaolinite lattice — forms. The mass loss in the process is 4.81%. It is known that kaolinite with no chemically bound water loses plasticity irreversibly.

At 400–100°C carbonates dissociate with carbonic acid being released, sulfides are oxidized with sulfur dioxide being formed, and organic mixtures burn up. These processes are accompanied by substantial mass loss, some increase of the porosity and decrease of volume, while the mechanical strength increases.

The exothermal effect in the temperature interval 978–1030°C is associated with the mullitization of kaolinite. At 1100°C structural rearrangement of meta-kaolinite with formation of the final stage of mullite occurs with heat being released:

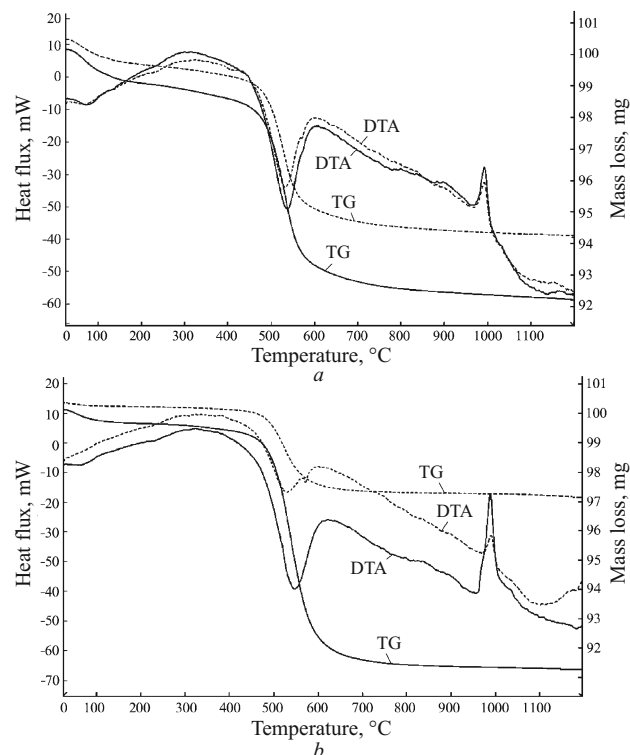


As temperature increases, the amount of mullite increases continually and reaches its highest value at 1250–1350°C. Prolonged soaking at temperatures above 1200°C has no effect on the increase of the mullite yield, but it does promote growth of mullite crystals.

Theoretically, all alumina present in kaolin should pass into mullite, but its yield in practice never corresponds to the theoretical value [3]. The total mass losses were 6.2%.

The effects described above have the same nature in both kaolins but the second endo effect for Dedovka kaolin (in natural and enriched form) is shifted to higher temperatures, and the accompanying mass losses are 2.84–8.03%. The exo effect occurring in the interval 960–1050°C and peaking at 988°C is characterized by a wider region of mullitization of kaolinite. The total mass losses were 3.21%.

The endo- and exothermal effects of enriched kaolin are sharper than in natural kaolin. This is explained by the absence of impurity minerals in them and a DTA curve close to that of pure kaolinite. For kaolins in unenriched form the effect bifurcates in the form of a step in the DTA curve at 570–580°C; this is due to the polymorphic transformation of quartz. The presence of a deeper endo effect on the curve for enriched kaolin is mainly due to the dehydration of the mineral and formation of a chemical compound with the composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  with a lattice that is ordered only in two directions. The exothermal effect at 980–990°C undergoes substantial changes; its area for enriched kaolin increases, and it is sharper because the process of dissociation of meta-kaolinite followed by joining of the structural units  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  into more or less extended groupings of amorphous substances and simultaneously increased equivalence of intra-tetrahedral bonds intensifies. A small amount



**Fig. 3.** Differential analysis plots of natural and enriched Sitnitsa (a) and Dedovka (b) kaolins: --- natural kaolin; — enriched kaolin.

of  $\gamma\text{-Al}_2\text{O}_3$  or mullite-like phase sometimes crystallizes in parallel. There are no clear arguments for an exothermal effect at 950–980°C, but most likely the energy source of exothermy is the free energy of meta-kaolinite [4].

It should be noted that if impurities with temperatures of thermal effects quite close to kaolinite are present in kaolins from the Belorussian deposits, then their presence is difficult of distinguish on a thermogram because of the high intensity of the thermal effects of the main mineral — kaolinite.

The principal physical-chemical properties of kaolin raw material from the Sitnitsa and Dedovka deposits are presented in Table 3.

Thus, it can be concluded that there is a large difference of the particle-size composition and plasticity number of kaolins from the deposits studied here; at the same time the elasticity and drying sensitivity indicators as well as the air shrinkage are not especially different. On the basis of the particle-size composition kaolins are a coarsely disperse raw material but at the same time the content of the finely disperse fraction and correspondingly the plasticity number are higher for Sitnitsa kaolin. Enrichment changes the elasticity indicator to values making it possible to place Sitnitsa and Dedovka kaolins in group II; this is also due to an increase of the sedimentation stability and ultimate fluidity of a kaolin suspension.

The kaolins from the deposits studied here do not meet the currently operative standards with respect to most indica-

**TABLE 3.** Principal Physical-Chemical Properties of Kaolin Raw Material

Kaolin deposit	Fine fractions content, %		Plasticity number	Drying sensitivity factor (according to Nosova)	Air shrinkage, %	Elastic indicator, g/cm <sup>3</sup>
	< 10 $\mu$ m	< 1 $\mu$ m				
Sitnitsa (natural)	27.58	11.70	6.86	0.13	4.1	0.05
Sitnitsa (enriched)	81.38	48.88	18.50	0.29	5.7	0.132
Dedovka (natural)	17.04	7.54	2.88	0.10	3.9	0.06
Dedovka (enriched)	55.12	25.96	12.60	0.16	4.8	0.144

tors. World experience in using kaolins shows that a kaolin enrichment technology can be developed for each particular deposit. This approach can be extended to kaolin in Belarus.

On the basis of the studies of the chemical-mineralogical features and the properties of kaolin raw materials from the Sitnitsa and Dedovka deposits, their quality was evaluated and the most effective methods for enriching them were recommended for each deposit. The choice of one or another method of enrichment is determined not only by the individual properties of kaolin from the deposits studied here but also by the possibility of using it in practice.

It is best to use different forms wet enrichment (electrolyte-free and in hydrocyclones), distinguished by the simplicity of the setup and high productivity [5, 6]. When using kaolins for white-burning articles chemical enrichment of Dedovka kaolin with lower iron content can be added to the method indicated. Bio-treatment of clarified kaolin by preparations of special bacteria is also promising; the activity of these bacteria extracts iron particles from the crystal lattice of silicates and removes them in the form of soluble compounds.

In summary, the use of various methods of enriching natural kaolins found in the Republic of Belarus makes it possible not only to expand the mineral raw materials resources

for the ceramic industry but also to implement the production of ecologically clean building and refractory materials on the basis of a potentially promising raw material — kaolins from the Republic of Belarus.

## REFERENCES

1. P. Z. Khomich, et al. (eds.), *Minerals of Belarus: 75th Anniversary of BelNIGRI, Ministry of Natural Resources and Environmental Protection of the Republic of Belarus, Belorussian Scientific-Research Institute of Geological Exploration* [in Russian], Adukatsyya i Vykhave, Minsk (2002), pp. 323 – 327.
2. M. E. Yakovleva, “Mineralogical-petrographic study of clays and kaolins,” in: *Proc. NIIsroikeraimika*, Moscow (1952), No. 6, pp. 100 – 125.
3. E. L. Rokhvager, *Building Ceramics* [in Russian], Stroiizdat, Moscow (1976).
4. I. A. Levitskii, et al., *IR Spectra and DTA Curves of Raw and Silicate Materials* [in Russian], Min. Obrazov. Resp. Belarus', BGTU, Izd. BGTU, Minsk (1999).
5. A. F. Galaburda and L. I. Shraiman, *Production of Kaolin* [in Russian], Gosstroizdat, Moscow (1958).
6. G. N. Malinovskii, et al., “On the possibility of increasing the degree of conditioning of kaolin raw materials found in the Republic of Belarus by different enrichment methods,” *Stroit. Nauka Tekhnika*, No. 4, 7 – 13 (2011).